1,123,521

PATENT SPECIFICATION 1,123,521

NO DRAWINGS.

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COMPLETE SPECIFICATION.

Jet Fuel Composition.

We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, residing at 135 East 42nd Street, New York New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel jet fuel composition and to a method for operating a turbine engine. The jet fuel of this invention comprises a hydrocarbon or a mixture of hydrocarbons in the gasoline and/or kerosene boiling ranges containing trimer acid in an amount effective to provide a fuel having a high level of anti-wear and water separation properties in addition to storage and thermal stability and other essential properties for these fuels.

Turbine engines are widely employed both in stationary power generating installations and for powering jet aircraft. These are high-powered engines and consume enormous amounts of the liquid hydrocarbon fuel being used. The fuel requirements of the engine are met with a fuel system having a high capacity fuel pump to deliver the required quantity of fuel.

Distillate petroleum hydrocarbon fractions in the gasoline and kerosene boiling ranges have essentially no lubricity or lubricating value. This is particularly true of light naphtha which is often economically attractive for fueling power turbines. In addition, the high solvent action of the noted fractions makes it extremely difficult if not impossible to maintain any lubricant on the surfaces that are constantly being washed by a large volume of fuel. It is for this reason that fuel pumps on turbine engines are subjected to serious wear which leads to failure of the fuel pump and shut down of the engine.

Turbine fuel compositions having anti-wear properties have been proposed heretofore to solve the problem of fuel pump wear. To date, no turbine fuel composition has been commercially adapted which combines outstanding anti-wear and water separation properties with an acceptable level of essential fuel properties. For example, it has not been possible as a practical matter to formulate such a turbine fuel having a Ryder gear test value of 1000 p.p.i., the minimum set by Pratt and Whitney (Registered Trade Mark) engine manufacturers without overloading the fuel with additives resulting in an inferior fuel having an unacceptable level of deposit and coke formation.

Light fuel compositions containing dimer and trimer acids are known, see U.S. Patent No. 2,632,695. This patent discloses light petroleum products containing dimer and trimer acids to prevent the formation of rust. For this purpose, the rust preventive used is one which is effective in concentrations not more than about 0.008 weight percent, an amount corresponding to not more than about 20 lbs./thousand barrels of fuel.

Trimer acids have also been proposed for jet fuel compositions designed to have anti-wear properties meeting the above-noted Pratt and Whitney specification. As previously proposed, a combination of trimer acid and an amine salt of a hydrocarbyl-substituted acid phosphate was found to meet the necessary anti-wear specification when each additive was employed in a concentration of 30 lbs./thousand barrels of fuel. At the present time, turbine engine manufacturers want only ashless additives in jet engine fuel compositions and this casts

doubt on the acceptability of the noted phosphorus-containing additive and fuel despite its high level of performance.

The fuels of th invention must meet many requirements before they can be used in turbine engines. In particular, the fuels must be thermally stable, have certain antioxidant properties and have a satisfactory Water Separometer Index. The latter propery is critical in fuels being employed in aircraft service because the entrainment of water in the fuel can lead to flame out or engine failure. The fuels must be noncorrosive to steel, copper and silver, the principal metals contacted by the fuel in service. The fuels should also be free of metallic compounds, sulfur compounds, phosphorus compounds and halogen compounds, because fuels containing additives with these elements may be corrosive or are believed to form corrosive combustion products.

It is an object of the present invention to provide a method for operating a turbine engine and a unique fuel composition which substantially reduces or overcomes the fuel pump wear problem encountered in the operation of turbine engines.

In accordance with this invention, a turbine engine equipped with a fuel system incorporating a fuel pump is run on a distillate hydrocarbon fraction in the gasoline and/or kerosene boiling ranges containing an effective wear inhibiting amount of trimer acid. In general, the novel fuel composition comprises a liquid hydrocarbon boiling in the gasoline and/or kerosene boiling ranges containing trimer acid in an amount ranging from 100 to 200 pounds per thousand barrels of fuel.

Throughout this Specification and the appended claims the term trimer acid refers to a conjugation product of three of the same molecules which are di-or polyethylenic fatty acids having from 16 to 22 carbon atoms.

The method of operating a turbine engine and the fuel composition of the invention are outstandingly effective for substantially reducing or eliminating fuel pump wear thereby overcoming what has been a serious limitation in the extended operation of such an engine. This performance has been realized by employing the noted additive alone at an unusually high aid critical concentration level surprisingly discovered to be effective for producing a fuel having excellent anti-wear and water separation properties.

The base fuel of the invention is a hydrocarbon or mixture of hydrocarbons in the gasoline and/or kerosene boiling ranges. Generally, such base fuels will boil in the range from about 90 to 500°F. Typical fuels for turbine engines include JP-3 a mixture of about 70 percent gasoline and 30 percent light distillate having a 90 percent evaporated point of 470°F., JP-4 a mixture of about 65 percent gasoline and 35 percent light distillate and JP-5, an especially fractionated kerosene having a high flash point and a low freezing point. Lead compounds, such at tetraethyl lead, are never employed in jet fuel compositions.

The fuel of the invention consists of a major portion of the base fuel and an effective wear-inhibiting amount of the trimer acid additive, an amount ranging from 100 to 200 pounds per thousand barrels of fuel. The preferred range for the trimer acid is from 110 to 140 pounds per thousand barrels of fuel. The broad range of 100 or 200 pounds per thousand barrels corersponds to approximately 0.04 to 0.08 weight percent of trimer acid in the fuel.

The trimer acids used may be fatty materials produced by subjecting unsaturated fatty acids having between 16 and 22 carbon atoms per molecule, and preferably about 18 carbon atoms, to condensation by moderate steam pressures of from 80 to 300 p.s.i.g. at temperatures from 260 to 360°C. for a period of from about 3 to 8 hours. Processes for forming these acids are set forth in such patents as U.S. 2,482,761, 2,631,979 and 2,632,695. Another method for preparing the trimer acid materials broadly comprises heating a short chain aliphatic alcohol ester of a diethylenic fatty acid at about 300°C. for several hours in an inert atmosphere. The resulting polymerized esters containing trimer acid material are then separated by distillation and hydrolyzed with hydrochloric acid or its equivalent. Fatty oils have also been heat polymerized and thereafter hydrolyzed to produce the polymer acids. The trimer acid is readily separated by distillation of by a solvent extraction process from the monomeric, dimeric and higher polymeric materials usually co-produced in the foregoing methods.

The trimer acids used in the present invention, although preferably conjugation products of three of the same molecules which are di-or polyethylenic, are also products of the combination of monoethylenic compounds and polyethylenic compounds, for instance, linoleic acid and oleic acids trimerized to become the trimer of linoleic and oleic acuds. It is essential to have at least one polyethylenic compound present in order to form the trimer acid.

Specific fatty acids useful for preparing trimer acid from the class of ethylenic carboxylic acids having from 16 to 22 carbon atoms include palmitoleic, oleic, linoleic and erucic acid. The preferred acid is linoleic acid on the basis of availability from which is produced the preferred trimer of linoleic acid. A trimer acid is produced commercially by polymerization of unsaturated C_{18} fatty acids by Emery Industries and consists of about 90 percent trimer acid, a fifty-four

carbon tribasic acid with a molecular weight of 845. All of the above acids are generally obtainable by hydrolyzing vegetable oils, such as linseed oil, soybean oil, cottonseed oil, and peanut oil. The use of trimer acid is critical for this invention as a related material, dimer acid, is deficient in the required anti-wear properties and gives a failing or unacceptable Water Separometer Index value to the turbine fuel of the invention.

Minor amounts of other additives may be employed in the turbine fuel although this is not essential to this invention. It is sometimes desirable to employ a hindered phenol in fuel compositions in an amount effective to impart improved oxidation inhibiting properties to the fuel. Effective phenols include 2,6-di-t-butyl-4-methyl phenol, 2,6-t-butyl phenol, 4,4[1]-methylene bis(2,6-di-t-butyl phenol), 2,6-di-t-butyl-4-di-methylaminoethyl-phenol, 2,4,6-tri-t-butylphenol, and 2,4-dimethyl-6-5-butyl phenol. When a phenol is employed, the amount is generally a concentration ranging from 1 to 30 pounds per barrel of fuel.

The following examples illustrate the practice of this invention. The base fuel employed in the Wear tests was an SO_2 extracted paraffinic fuel described below:

TABLE I
INSPECTION TESTS ON BASE FUEL

Gravity, °API	46.9
Distillation Temp. °F.	
IBP	378
EP	485
Sulfur, %	0.002
Freezing Point, °F.	−48
Heat of Combustion B.T.U./lb.	18,686
Luminometer No.	82.8
Aromatic Content, %	2

The anti-wear properties of the fuel of the invention was determined in the Ryder Gear Test. This test is described in U.S. 3,134,737 and the results are set forth in Table II below:

TABLE II
RYDER ANTI-WEAR TESTS

Run	Trimer Acid, PTB	Ryder Gear Test, ppi
1.	0 (base fuel)	443
2.	90	885
3.	120	1190

It can be seen that the critical Ryder Gear Test value of 1000 p.p.i. is realized at a minimum concentration of about 100 PTB of the trimer acid.

The Water Separometer Index (W.S.I.) value of the fuel of the invention was determined according to Federal Test Method 791a-3256 entitled "Determination of Water Separation Properties of Aviation Turbine Fuels". According to this test, 2,000 cc. of fuel plus 2 cc. of water are circulated in a closed system by means of a small gear pump having an output rating of 400 cc. per minute. The micro-ammeter in the apparatus is set before water addition so that the Water Separometer Index value of the base fuel without water is 100. Fuel and water are circulated for five minutes to insure complete mixing of the water-fuel mixture. A portion of this fuel mixture is then circulated through a glass system at a rate of 150 cc./min. This effluent passes through a glass fiber filter coalescer and then through a glass tube equipped with a light and photoelectric cell for determining the light transmission upon which the Water Separometer Index is based. The Water Separometer Index value of the circulated fuel-water mixture is taken in the photoelectric measuring device after the mixture has been passed through the glass filter. The higher the Water Separometer Index the better the fuel is with respect to its water separation properties. A fuel must have a minimum value of 85 to pass the military specification MIL-J-5624F for these fuels. Additive concentrations are shown as PTB, pounds of additive per 1000 barrels of fuel. (One barrel equals 42 U.S. gallons.)

TABLE III
WATER SEPAROMETER INDEX TEST

Additive, PTB		Water Separometer Index (*)
1. None		98(1)
2. None		98(2)
3. Trimer Acid,	90 PTB	97(1)
3a. Trimer Acid,	100 PTB	97(3)
4. Trimer Acid,	120 PTB	98(2)
5. Dimer Acid,	20 PTB	79(1)
6. Dimer Acid,	100 PTB	66(3)

(*) 85 is minimum value to pass.
(1) Fuels consisted of 90% Udex (Registered Trade Mark) Raffinate and 10% Xylene.
(2) Fuel consisted of 100% Udex (Registered Trade Mark) Raffinate.
(3) Light Naphtha.

The turbine fuel of the invention possesses outstanding anti-wear and Water Separometer Index properties as well as good thermal stability and other properties which are essential in a turbine fuel. This fuel overcomes the problem of fuel pump wear in the fuel system of a turbine engine without the use of additives containing metal components, sulfur compounds, or halogen

compounds which promote corrosion in turbine fuels.

WHAT WE CLAIM IS:—

1. A jet fuel composition comprising a mixture of hydrocarbons boiling in the gasoline and/or kerosene boiling ranges containing from 100 to 200 pounds per thousand barrels of fuel of trimer acid.

2. A jet fuel according to Claim 1 boiling in the range from 90—500°F.

3. A jet fuel according to Claim 1 containing from 110 to 140 pounds of trimer acid per thousand barrels of fuel.

4. A jet fuel according to Claim 1 in which said trimer acid is derived from polymerized linoleic acid.

5. A method of operating a turbine engine which comprises supplying to and burning in said engine a jet fuel composition comprising a mixture of hydrocarbons boiling in the gasoline and/or kerosene boiling ranges containing from 100 to 200 pounds per thousand barrels of fuel of trimer acid.

6. A method according to Claim 5 in which said jet fuel boils in the range of 90 to 500°F.

7. A method according to Claim 5 in which said trimer acid is derived from polymerized linoleic acid.

8. A method according to Claim 5 in which said jet fuel contains 110 to 140 pounds of trimer acid per thousand barrels of fuel.

9. A jet fuel composition according to Claim 1 and substantially as hereinbefore described with reference to any of the Examples.

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